

Superconductivity at 33 K in “111” single crystals at ambient pressure

T.-L. Xia, J. B. He, D. M. Wang, and G. F. Chen*

Department of Physics, Renmin University of China, Beijing 100872, P. R. China

(Dated: February 3, 2010)

Abstract

We have successfully grown single crystalline NaFeAs with cobalt or phosphor doping. Bulk superconductivity occurs in NaFe_{0.95}Co_{0.05}As at 19 K while much higher transition temperature is observed in NaFeAs_{0.8}P_{0.2}, in which the T_c of 33 K is even higher than the highest value realized by applying pressure in NaFeAs and all other isoelectronic element substituted samples. We discuss these behaviours by comparison with 122 and 1111 systems. We hope that our findings will help improve our understanding of iron-based superconductivity.

PACS numbers: 74.70.Xa, 74.25.F-, 74.25.Op

*Electronic address: genfuchen@ruc.edu.cn

Since the discovery of superconductivity at 26 K in iron-based oxypnictide $\text{LaFeAsO}_{1-x}\text{F}_x$, [1] doping at different sites in the corresponding parent compound LnFeAsO ($\text{Ln}=\text{Lanthanide}$) with different elements has been extensively attempted to get new superconductors, including isoelectronic substitution of smaller lanthanide ions for bigger ones leading the T_c in the iron-based superconductors firstly to be higher than 40 K, [2, 3] oxygen deficiency in the 1111 system to give higher transition temperature up to 55 K, [4] and the carriers doping with different types at different sites inducing superconductivity. [5–7] Soon after the discovery of above so called 1111 system with ZrCuSiAs -type structure, AFe_2As_2 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$) with ThCr_2Si_2 -type structure (122 system) were found to superconduct once the carriers are appropriately introduced [8–13] or the pressure was applied. [14, 15] K doping at A site, [8–11] P doping at As site [16] and Co doping at Fe site [12, 13] all lead to superconductors, in which the highest T_c is 38 K in $\text{Ba}_{1-x}\text{K}_x\text{FeAs}$. [8]

As for 111 system, the investigation on LiFeAs presents superconductivity without any hint on structural or magnetic orders. [17–19] The same situation holds for NaFeAs before we present the high quality data on single crystalline NaFeAs , where three successive transitions corresponding to structural, magnetic and superconducting transitions have been observed in the resistivity and magnetic susceptibility curves [20] and later confirmed by neutron scattering and muon-spin rotation results. [21, 22] The neutron scattering results indicate that the spin within ab plane is ferromagnetically aligned along b axis and antiferromagnetically along a axis, while in c directions it is antiferromagnetically coupled. Up to now, there is no reports on the study of magnetic structure in LiFeAs , but Li *et al.* did the first-principles calculations and predicted the stripe antiferromagnetic ground state with easy axis of magnetization along the b direction of the magnetic unit cell. [23] Thus, 111 system is believed to be the same as 122 and 1111 systems in their magnetic structures. But if we take into account the position of Na or Li ions with respect to the FeAs block, we see difference between 111 system and 122 or 1111 system. Li or Na takes the position of $\text{Fe}(2)$ in the compound of Fe_2As (PbFCl or Cu_2Sb structure) and it is assumed to be possible that Li or Na directly interacts with the 5 neighboring As. The delicate difference in their crystal structures may be one possible origin for their slightly different electronic properties between LiFeAs (NaFeAs) and 1111 or 122 systems. To elucidate this problem, NaFeAs is doped with Co or P to see if the results can provide us some hints on the difference or common features between their properties and other doped 122 or 1111 system and further supply additional

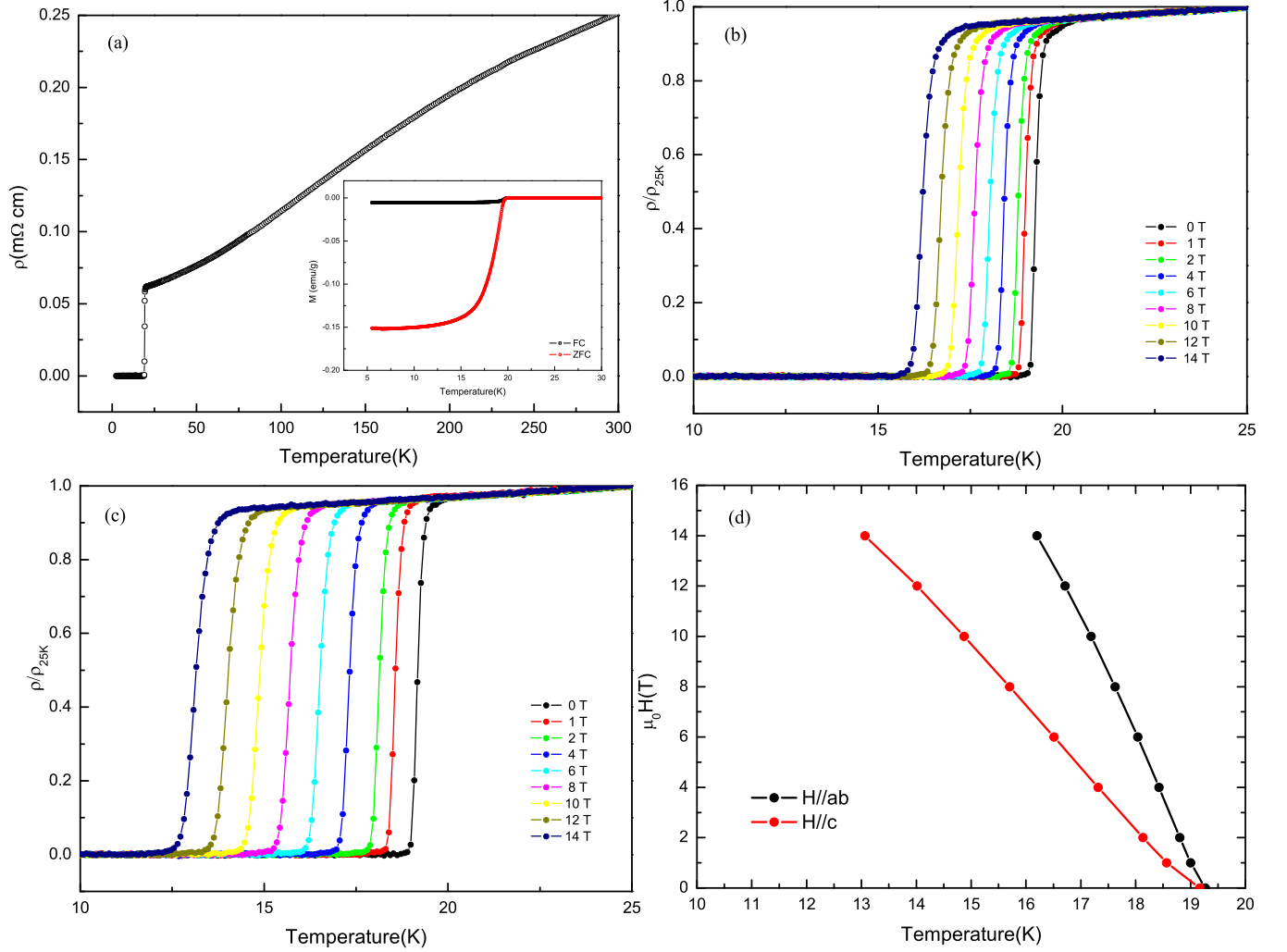


FIG. 1: (Color online) (a) Temperature dependence of the electrical resistivity for a NaFe_{0.95}Co_{0.05}As single crystal in zero field up to 300 K. The inset shows the temperature dependent magnetization data under ZFC and FC conditions with $H=10$ Oe. (b) Temperature dependence of the resistivity normalized to resistivity at 25 K at fields up to 14 T with $H||ab$. (c) Temperature dependence of the resistivity normalized to resistivity at 25 K at fields up to 14 T with $H||c$. (d) The upper critical field of NaFe_{0.95}Co_{0.05}As single crystal for $H||ab$ and $H||c$.

data to understand the mechanism of superconductivity in Fe-Pnictide superconductors.

Both kind of samples were grown employing self-flux method. NaAs, FeAs, Fe₂As, CoAs, FeP, and Fe₂P were firstly synthesized as precursors in the same way as reported before[20]. Mixtures of above raw materials with nominal compositions NaFe_{0.95}Co_{0.05}As and NaFeAs_{0.8}P_{0.2} were loaded into alumina tubes and then sealed into Ta tubes with Ar

under the pressure of 1.5 atom., then the sealed Ta tubes were vacuum sealed into quartz tubes. The samples were put in box furnace and heated to 1170 °C slowly and held there for a few hours before the temperature was decreased very slowly. The grown crystals have the form of platelets with shiny facets. The dimensions of the crystals are not so large as 122 crystals. The maximum size of the grown and mechanically cleaved samples are $\sim 5 \times 5 \times 0.2 \text{ mm}^3$. Their electronic and magnetic properties were measured on a Quantum Design physical property measurement system (PPMS) with the VSM option provided.

Figure 1(a) shows the temperature dependence of resistivity for $\text{NaFe}_{0.95}\text{Co}_{0.05}\text{As}$ crystal between 2.2 K and 300 K. No other anomalies are observed except for the superconducting transition at 19 K (Here T_c is defined as the temperature where zero resistivity is achieved), which means no transitions related to magnetic or structural orders exist as found in $\text{Na}_{1-\delta}\text{FeAs}$ single crystals.[20] The result is consistent with previous reports on Co doped NaFeAs polycrystalline samples,[24] where the magnetic and structural transitions are absent when the carriers like Co or Ni are introduced into the system and the bulk superconductivity is established. The inset of Fig. 1(a) shows the temperature dependence of the magnetization in the single crystal of $\text{NaFe}_{0.95}\text{Co}_{0.05}\text{As}$ under the conditions of zero field cooling (ZFC) and field cooling (FC) at $H=10 \text{ Oe}$. The perfect diamagnetism indicates the bulk superconductivity. Taking into account the T_c s in other Co doped system like 22 K in $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$, 20 K in $\text{SrFe}_{2-x}\text{Co}_x\text{As}_2$, 18-19 K in $\text{CaFe}_{2-x}\text{Co}_x\text{As}_2$ and 10-24 K in $\text{LnFe}_{1-x}\text{Co}_x\text{AsO}$ ($\text{Ln}=\text{La}, \text{Ce}, \text{Nd}, \text{Sm} \text{ etc.}$), the transition temperature of 19 K is at the same level and consistent with previous reports on polycrystalline Co-doped NaFeAs .[24] Later in this paper we find P-doped NaFeAs presents much higher T_c compared with above values and it is even higher than all the T_c s realized through Co or P doping in their parent compounds in 122 or 1111 system.

Figure1 (b) and (c) show the behavior of resistivity of $\text{NaFe}_{0.95}\text{Co}_{0.05}\text{As}$ in external magnetic field up to 14 T. In Fig. 1(b), the applied field is within the ab plane ($H\parallel ab$) while in Fig. 1(c) the applied field is parallel to the c axis ($H\parallel c$). We see the superconducting transition is suppressed in both conditions but the effect of magnetic field is much larger when the field is applied along the c axis of the single crystals in stead of within the ab plane. The corresponding upper critical field H_{c2} as a function of temperature obtained from a determination of the midpoint of the resistive transition is plotted in Fig. 1(d). The curves are steep with slopes $-dH_{c2}/dT|_{T_c}=4.7 \text{ T/K}$ for $H\parallel ab$ and $-dH_{c2}/dT|_{T_c}=2.4 \text{ T/K}$ for $H\parallel c$. According

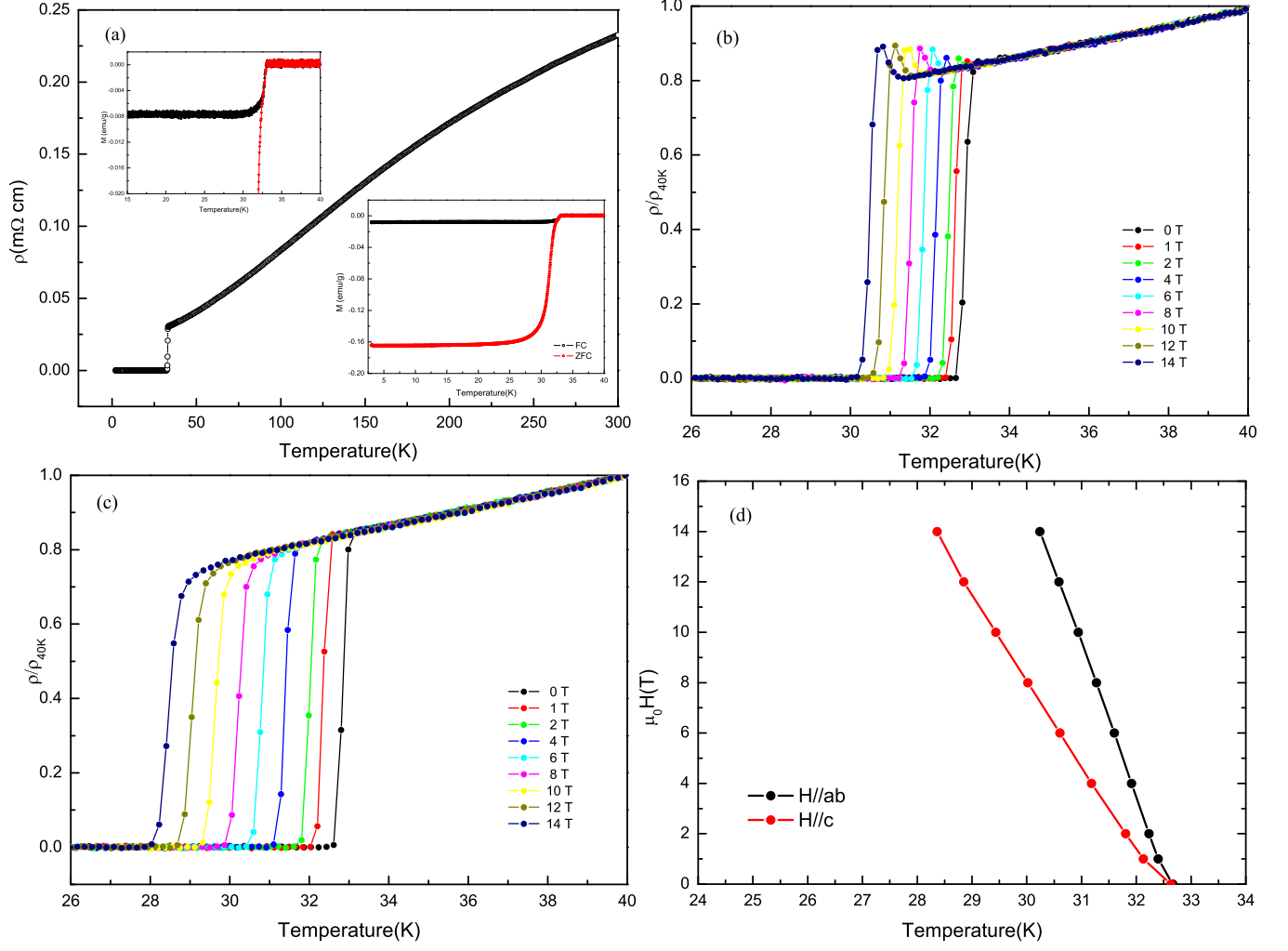


FIG. 2: (Color online) (a) Temperature dependence of the electrical resistivity for a $\text{NaFeAs}_{0.8}\text{P}_{0.2}$ single crystal in zero field up to 300 K. The down right inset shows the temperature dependent magnetization data under ZFC and FC conditions with $H=10$ Oe. The up left inset is the enlarged part for M-T curve. (b) Temperature dependence of the resistivity normalized to resistivity at 40 K at fields up to 14 T with $H||ab$. (c) Temperature dependence of the resistivity normalized to resistivity at 40 K at fields up to 14 T with $H||c$. (d) The upper critical field of $\text{NaFeAs}_{0.8}\text{P}_{0.2}$ single crystal for $H||ab$ and $H||c$.

to the Werthamer-Helfand-Hohenberg (WHH) formula[25] $H_{c2}(0) = -0.69(dH_{c2}/dT)T_c$ and taking 19 K as T_c , the upper critical fields are estimated to be $H_{c2}^{ab}=62$ T and $H_{c2}^c=31$ T. The ratio of H_{c2}^{ab}/H_{c2}^c is about 2 which means the anisotropy is not so large even the upper critical fields are high.

The above results on electronic properties in Co-doped NaFeAs are consistent with that of Co-doped 122 or 1111 systems. We know that phosphor doping in BaFe_2As_2 induces superconductivity with $T_c=30$ K, much higher than the $T_c=22$ K of Co-doped BaFe_2As_2 . When we dope NaFeAs with P, our results do show clear transition temperature high up to 33 K. It is clearly shown both in the resistivity curve (Fig. 2(a)) and magnetization data (The inset of Fig. 2(a)). The superconducting transition is very sharp with the transition width smaller than 1 K. What is the cause of such a high transition temperature remains an open question. Mizuguchi *et al.* proposed in their report that the anion height is crucial in determining the T_c of the iron-based superconductors.[26] In P-doped NaFeAs, the Fe has the valence of 2+, and no nominal carriers are introduced into the iron layer, which may not cause disorder in the iron layer. But according to their strict requirement, no dopings can be done on anion site either, ie. no substitution of P for As should be done if the rules are satisfied before P-doped NaFeAs is put on the symmetric curve they proposed.

On the other hand, regular tetrahedron of FeAs_4 lattices in the FeAs block are believed to be one key point in achieving higher T_c [27, 28]. More and more results are consistent with the prediction and obey the rule. In 111 system, pressure effect on LiFeAs is systematically studied, and T_c decreases with increasing pressure.[29] The lattice parameters are summarized based on Rietveld refinement and it is found that the FeAs_4 tetrahedron is highly distorted and the pressure further enhances the distortion so the T_c decreases. As for NaFeAs, the T_c of NaFeAs is 23 K,[20] and refinement results show us NaFeAs possesses a more regular tetrahedron with the basic difference that the radii of Na is bigger than that of Li and it forms a less distorted environment.[22] The P-doped NaFeAs superconducts at 33 K, so we believe that the FeAs_4 tetrahedron here is more regular than that in Na-deficiency polycrystalline NaFeAs.[22] We should emphasize the T_c is the highest in all Co-doped or isoelectronic element-doped systems. In previous report on NaFeAs polycrystalline samples, the maximum T_c of 31 K is observed when the pressure of 3.0 GPa is applied.[30] As we know the pressure effect on iron-based superconductors are complex with two major categories: one type is that pressure enhances the T_c of the samples while another is that the pressure firstly enhances then suppresses the T_c . These behaviors are intimately related to the lattice parameters and configuration of FeAs_4 tetrahedron. Considering such effect, we expect possible higher T_c to be realized in the work studying the pressure effect on P-doped NaFeAs crystals. Further work on the lattice parameters and pressure effect on the P-doped

NaFeAs are in progress.

Anisotropy of electronic transport properties have also been studied and the results are shown in Fig.2 (b) and (c). The similar behavior of field on the transition is observed. When the magnetic field is applied within ab plane, the transition is less affected than the situation when the field is applied along the c axis. The corresponding values are $-dH_{c2}/dT|_{T_c}=6.0$ T/K for $H\parallel ab$ and $-dH_{c2}/dT|_{T_c}=3.4$ T/K for $H\parallel c$. Taking 33 K as T_c and using WHH formula, we get the corresponding upper critical fields as high as $H_{c2}^{ab}=137$ T and $H_{c2}^c=77$ T. Such high critical fields and low anisotropy ratio ($137/77=1.78$) are comparable to other 122 system and may have the potential for future applications in the superconducting devices. Recently, Chong *et al.* summarized the results of high field study on 122 and 111 samples and concluded that the hole-doped system have higher upper critical fields > 100 T compared to the electron-doped system, while those of strain or pressure induced superconductivity have similar upper critical fields as in the electron-doped system.[31] They did the measurements on single crystalline $\text{BaFe}_2\text{As}_{1.36}\text{P}_{0.64}$ ($T_c=31$ K) and estimated the upper critical fields as $H_{c2}^{ab}=77$ T and $H_{c2}^c=36$ T. Our results of upper critical fields with $H_{c2}^{ab}=137$ T and $H_{c2}^c=77$ T are the largest among the 111 and 122 systems except for those in hole-doped cases and it is the first exception of samples with upper critical field >100 T which is non-hole-doped system. Previous high magnetic field experiments on $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$ show nearly isotropic superconductivity in that system[32] and later the same conclusion is drawn by other high magnetic field experiments on $\text{Ba}(\text{Fe},\text{Co})_2\text{As}_2$. [33, 34] So, it is necessary to do the high magnetic field experiments in the 111 system and the work is in progress.

To summarize, we have grown the high quality single crystals of NaFeAs with Co- and P-doping. We find that the superconductivity occurs at ambient pressure with T_c up to 33 K in $\text{NaFeAs}_{0.8}\text{P}_{0.2}$. We emphasized that the value of T_c is the highest in 111 system and in all other isoelectronic element substituted 122 or 1111 system. The upper critical fields are estimated high up to 77 T with $H\parallel c$ and 137 T with $H\parallel ab$ for $\text{NaFeAs}_{0.8}\text{P}_{0.2}$, which are also the highest in 122 and 111 systems except for those in hole-doped cases. We believe that these results provide important information for establishing a theory to understand the superconductivity in the iron-based superconductor.

The work is supported by the National Science Foundation of China and the 973 project

of the Ministry of Science and Technology of China.

- [1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
- [2] G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. **100**, 247002 (2008).
- [3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) **453**, 761 (2008).
- [4] Z. A. Ren, G. C. Che, X. L. Dong, J. Yang, W. Lu, W. Yi, X. L. Shen, Z. C. Li, L. L. Sun, F. Zhou, and Z. X. Zhao, Europhys. Lett. **83**, 17002 (2008).
- [5] H. H. Wen, G. Mu, L. Fang, H. Yang, and X. Y. Zhu, Europhys. Lett. **82**, 17009 (2008).
- [6] C. Wang, L. J. Li, S. Chi, Z. W. Zhu, Z. Ren, Y. K. Li, Y. T. Wang, X. Lin, Y. K. Luo, S. Jiang, X. F. Xu, G. H. Cao, and Z. A. Xu, Europhys. Lett. **83**, 67006 (2008).
- [7] A. S. Sefat, A. Huq, M. A. McGuire, R. Y. Jin, B. C. Sales, D. Mandrus, L. M. D. Cranswick, P. W. Stephens, and K. H. Stone, Phys. Rev. B **78**, 104505 (2008).
- [8] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).
- [9] G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, P. Zheng, N. L. Wang, and J. L. Luo, Chin. Phys. Lett. **25**, 3403 (2008).
- [10] K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y. Y. Xue, and C. W. Chu, Phys. Rev. Lett. **101**, 107007 (2008).
- [11] N. Ni, S. L. Bud'ko, A. Kreyssig, S. Nandi, G. E. Rustan, A. I. Goldman, S. Gupta, J. D. Corbett, A. Kracher, and P. C. Canfield, Phys. Rev. B **78**, 014507 (2008).
- [12] A. S. Sefat, R. Y. Jin, M. A. McGuire, B. C. Sales, D. J. Singh, and D. Mandrus, Phys. Rev. Lett. **101**, 117004 (2008).
- [13] A. Leithe-Jasper, W. Schnelle, C. Geibel, and H. Rosner, Phys. Rev. Lett. **101**, 207004 (2008).
- [14] M. S. Torikachvili, S. L. Budko, N. Ni, and P. C. Canfield, Phys. Rev. Lett. **101**, 057006 (2008).
- [15] M. S. Torikachvili, S. L. Bud'ko, N. Ni, and P. C. Canfield, Phys. Rev. B **78**, 104527 (2008).
- [16] Z. Ren, Q. Tao, S. Jiang, C. Feng, C. Wang, J. Dai, G. Cao, and Z. Xu, Phys. Rev. Lett. **102**, 137002 (2009).
- [17] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin,

- Solid State Communications **148**, 538 (2008).
- [18] M. J. Pitcher, D. R. Parker, P. Adamson, S. J. C. Herkelrath, A. T. Boothroyd, and S. J. Clarke, Chem. Commun. 5918, (2008).
 - [19] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu, and A. M. Guloy, Phys. Rev. B **78**, 060505(R) (2008).
 - [20] G. F. Chen, W. Z. Hu, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 102, 227004 (2009).
 - [21] S. Li, C. de la Cruz, Q. Huang, G. F. Chen, T. L. Xia, J. L. Luo, N. L. Wang, and P. Dai, Phys. Rev. B 80, 020504(R) (2009).
 - [22] D. R. Parker, M. J. Pitcher, P. J. Baker, I. Franke, T. Lancaster, S. J. Blundell, and S. J. Clarke, Chem. Commun. 2189 (2009).
 - [23] Z. Li, J. S. Tse, and C. Q. Jin, Phys. Rev. B 80, 092503 (2009).
 - [24] D. R. Parker, M. J. P. Smith, T. Lancaster, A. J. Steele, I. Franke, P. J. Baker, F. L. Pratt, M. J. Pitcher, S. J. Blundell, and S. J. Clarke, arXiv:0909.0417.
 - [25] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. 147, 295 (1966)
 - [26] Y. Mizuguchi, Y. Hara, K. Deguchi, S. Tsuda, T. Yamaguchi, K. Takeda, H. Kotegawa, H. Tou and Y. Takano, arXiv:1001.1801.
 - [27] J. Zhao, Q. Huang, C. de la Cruz, S. L. Li, J. W. Lynn, Y. Chen, M. A. Green, G. F. Chen, G. Li, Z. Li, J. L. Luo, N. L. Wang, and P. C. Dai, Nat. Mater. 7, 953 (2008).
 - [28] C. H. Lee, A. Iyo, H. Eisaki, H. Kito, M. T. Fernandez-Diaz, T. Ito, K. Kihou, H. Matsuhata, M. Braden, and K. Yamada, J. Phys. Soc. Jpn. 77, 083704 (2008).
 - [29] M. Mito, M. J. Pitcher, W. Crichton, G. Garbarino, P. J. Baker, S. J. Blundell, P. Adamson, D. R. Parker, and S. J. Clarke, J. Am. Chem. Soc. 131, 2986 (2009).
 - [30] S. J. Zhang, X. C. Wang, Q. Q. Liu, Y. X. Lv, X.H. Yu, Z.J. Lin, Y. S. Zhao, L. Wang, Y. Ding, H. K. Mao and C. Q. Jin, Europhys. Lett. 88, 47008 (2009).
 - [31] S. V. Chong, S. Hashimoto and K. Kadowaki, arXiv:0908.3284.
 - [32] H. Q. Yuan, J. Singleton, F. F. Balakirev, S. Baily, G. F. Chen, J. L. Luo, N. L. Wang, Nature 457, 565 (2009)
 - [33] M. A. Tanatar, N. Ni, C. Martin, R. T. Gordon, H. Kim, V. G. Kogan, G. D. Samolyuk, S. L. Budko, P. C. Canfield, and R. Prozorov, Phys. Rev. B **79**, 094507 (2009).
 - [34] A. Yamamoto, J. Jaroszynski, C. Tarantini, L. Balicas, J. Jiang, A. Gurevich, D. C. Larbalestier, R. Jin, A. S. Sefat, M. A. McGuire, B. C. Sales, D. K. Christen, and D. Mandrus,

Appl. Phys. Lett. 94, 062511 (2009)